Colored Dissolved Organic Matter in Sediments and Seagrass Beds and its Impact on Shallow Water Benthic Optical Properties

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LONG TERM GOALS

The optical properties of shallow water coastal environments are a complex function of physical and biogeochemical processes occurring both in sediments and in the water column. Developing models of the optical properties of these environments requires further knowledge of the processes affecting light alteration and modification by biogeochemical reactions in the surficial sediments and at the sediment-water interface. The goal of this proposal is to examine one aspect of this problem, namely the impact of dissolved organic matter (DOM) in sediment pore waters on benthic optical properties.

OBJECTIVES

In this proposal I am examining the processes affecting the production of colored and fluorescent dissolved organic matter (CDOM) in sediment pore waters, the mechanism(s) by which this material may be transported out of the sediments, and the impact of pore water CDOM on the optical properties of the shallow water benthos (i.e., both the sediments, the sediment-water interface and the waters overlying the sediment, including the benthic boundary layer).

APPROACH

To address these questions I am using a combination of field measurements and experiments, all carried out in close cooperation and coordination with other funded CoBOP researchers. These include: 1. determining bottom water concentrations and sediment (pore water) profiles of CDOM; 2. examining DOM and CDOM that is easily extractable from sediment particles; 3. determining sediment profiles of other relevant solid phase and dissolved constituents (to characterize the basic biogeochemical properties of the sediments); 4. examining benthic fluxes of CDOM; 5. carrying out experiments to determine the "optical fate" of sediment CDOM in the waters at or just above the sediment surface (i.e., once the pore water CDOM is transported out of the sediments by any of the processes discussed above).

Studies of CDOM that is easily extractable for sediments has been added to our research efforts based on results obtained during our first LSI field studies - namely that relatively large amounts of optically-active DOM can be desorbed from LSI sediments using a simple seawater extraction procedure (~10 gr of wet sediment is extracted with 20 ml of filtered seawater, using sequential 10 ml extractions for 1 hr each at 4°C; see **Results** for further details).

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CDOM from pore waters and bottom waters is being characterized both chemically and optically. Chemical analyses involve measuring total dissolved organic carbon and nitrogen, along with total dissolved carbohydrates. CDOM is characterized optically by measuring its UV/Vis absorption spectrum and using fluorescence excitation-emission matrix spectroscopy. The combination of these two techniques provides complimentary information on the optical properties of DOM in seawater, since many CDOM compounds in natural waters absorb light without fluorescing. Similar approaches are also used to characterize easily extractable CDOM.

In the first field campaign at LSI (May 1998) we experienced difficulties in collecting the large diameter sediment cores used in the pressurized core barrel (PCB) pore water collection technique we have used in previous sediment studies (e.g., Burdige and Gardner, 1998). Therefore, on-site we built in situ pore water sippers for use in our first LSI studies. Essentially, these sippers consist of a series of teflon tubes of different lengths (1,2, 5 and 10 cm) with a small piece of porous polypropylene rod on the end of each tube (as per our PCB samplers). These tubes are mounted on a small plate and attached to sampling syringes with barbed Luer-lock fittings that screw into the plate. The samplers are pushed into the sediments by divers and, as with our PCB samplers, pore water samples are obtained by pulling a vacuum on the syringe attached to each sampling tube. These pore water sippers were subsequently modified for ease of use underwater, and the modified sippers were used successfully at LSI in January and May/June 1999. Both versions of these sippers appear to obtain reliable pore water samples.

Benthic CDOM fluxes were determined using diver-emplaced in situ benthic flux chambers. In the most recent LSI field efforts (May/June 1999) this approach was carried out successfully at two study sites (the Channel Marker site and the Norman's Grapestones sediment site) and we are currently analyzing samples collected from these studies. To quantify other important biogeochemical processes in these sediments such as calcite dissolution and rates of sediment carbon oxidation we also determine the fluxes of the following chemical constituents in these studies: TCO_2 (total dissolved inorganic carbon), alkalinity, nitrate + nitrite and ammonium (see Burdige and Homstead,1994, and Berelson et al.,1996, for further details).

Our work is carried out by myself (as PI of the project), Mr. Kip Gardner (a research technician in my lab), Dr. Wenhao Chen (a post-doctoral research associate who worked on this project until August 1998), and Mr. Scott Kline (a Ph.D student working with me on this project who plans to use his work here as a part of his Ph.D. dissertation).

WORK COMPLETED

Work completed this year has involved two sampling trips to the major CoBOP field sites in the sediments around Lee Stocking Island (Exuma Islands, the Bahamas). We have completed all analyses of samples collected at LSI in January, 1999 and are currently completing the analysis of samples collected in May/June 1999.

RESULTS

Specific observations made during our first set of studies at Monterey Bay and Lee Stocking Island (LSI) include the following:

1. Bottom waters around LSI contain relatively elevated levels of DOC (~80 - 120 μM), although this material is not very optically-active (e.g., it has low fluorescence, absorbance, and high S values). Photobleaching may be a possible explanation for these observations.

2. Low levels of DOC are found in most LSI sediment pore waters, with very small gradients across the sediment-water interface (e.g., Figure 1). These observations suggest that rates of organic matter remineralization in these LSI sediments are very low, and inorganic pore water data (alkalinity, TCO_2 and ammonium concentrations) from these sites are consistent with this suggestion (results not shown here). Seagrass sediments (both in Monterey Bay and at the LSI Channel Marker site) show the highest pore water DOC concentrations (Figure 1).

3. Pore water DOM at both LSI and Monterey Bay may be a bit more optically-active than that in bottom waters, since there appear to be slightly larger pore water gradients in fluorescent DOM as compared to gradients of total DOC (e.g., see Figure 1). In terms of CDOM fluorescence and UV/Vis absorbance, CDOM in LSI and Monterey Bay sediment pore waters looks similar to pore water CDOM from other marine environments we have studied (e.g., Chesapeake Bay and the mid-Atlantic shelf/slope break).

4. Sediment extracts from LSI sediments contain elevated levels of optically-active DOC. Compared to ambient Exuma Sound seawater these extracts are enriched from 3 to 150 times in DOC or fluorescent CDOM. These extracts contain very high levels of protein-like fluorescence (primarily due to tryptophan fluorescence) as well as humic-like fluorescence. Based on arguments presented elsewhere (Lakowicz, 1983; Chen and Burdige, 1998; Mayer et al., 1999) the occurrence of tryptophan fluorescence suggests that some of this extractable CDOM may be fresh/labile organic matter associated with biofilms and/or benthic biomass (algal or bacterial). There also appear to be significant differences among sites in both the amounts of extractable organic matter (Figure 2, upper panel) as well as its optical activity (as expressed by the peak A/OC or peak T/OC ratios in the lower panel in Figure 2). Comparing these results with typical TOC concentrations in organic-poor carbonate sediments suggest that up to ~30% of the TOC in such sediments could be this easily extractable material. Furthermore, these results also suggest another potential mechanism by which sediments can add CDOM to the water column, that is through desorption associated with sediment resuspension events.

In our CoBOP studies we have collected data on three LSI sampling trips (May 1998, January 1999, May.June 1998) and three Monterey Bay sampling trips (November 1997, 1998 and 1999). These data sets include: bottom water and sediment pore water profiles of CDOM concentrations and properties (e.g., S values, Ex_{max} and Em_{max} values for fluorescence peaks), ancillary inorganic and organic sediment profiles (e.g., pore water DOC, alkalinity, sulfate); data on easily extractable CDOM from LSI sediments; results from LSI benthic flux studies. To date, we have only sent the data from our first LSI sampling trip to the CoBOP data base. The remaining data will be sent to the data base when the data formatting issues discussed at the most recent CoBOP PI's meeting are resolved. As of now, we have not yet formally received or used data from other CoBOP PI's, although I anticipate using/needing data from a number of CoBOP PI's in the on-going interpretation of our results (see **Related Projects** for further details).

IMPACT

The fluorescence data collected so far have been useful in terms understanding the controls on DOM cycling in marine sediment pore waters (e.g., Burdige and Gardner, 1998; Chen and Burdige, 1998; Burdige, 1999), and in examining the extent to which coastal sediments are sources of CDOM to coastal

waters. Studies of the fluorescence of easily extractable organic matter may also prove useful in understanding the controls on the optical properties of different sediment types.

TRANSITIONS

Based on discussions at the recent CoBOP review meeting, our results appear to be of interest to many of the other CoBOP investigators. In particular, during the most recent LSI field campaign (May/June 1999) we carried out side-by-side sediment sampling/analysis of pore water CDOM with R. Zanfeld and E. Boss (OSU), using our techniques and a diver-operated version of the WET Labs AC-9, modified to draw pore waters out of the sediments for in situ analysis. This comparison was carried out at two distinctly different sediment sites, the organic-poor Ooid Shoals site and the more organic-"rich" seagrass sediments at the Channel Marker site. Such a comparison will likely prove useful and important in making linkages between the more chemically-based CDOM measurements we are carrying out and the in situ determination of CDOM made using instruments such as the AC-9.

RELATED PROJECTS

The efforts are closely related to several other CoBOP projects, including those of M. Allison, R. Wheatcroft, A. Decho, F. Dobbs/L. Drake, R. Zimmerman, P. Reid, C. Mazel and R. Zanfeld/E. Boss. We have begun to explore these areas of common interest in previous CoBOP field efforts and will continue to do so in future field studies.

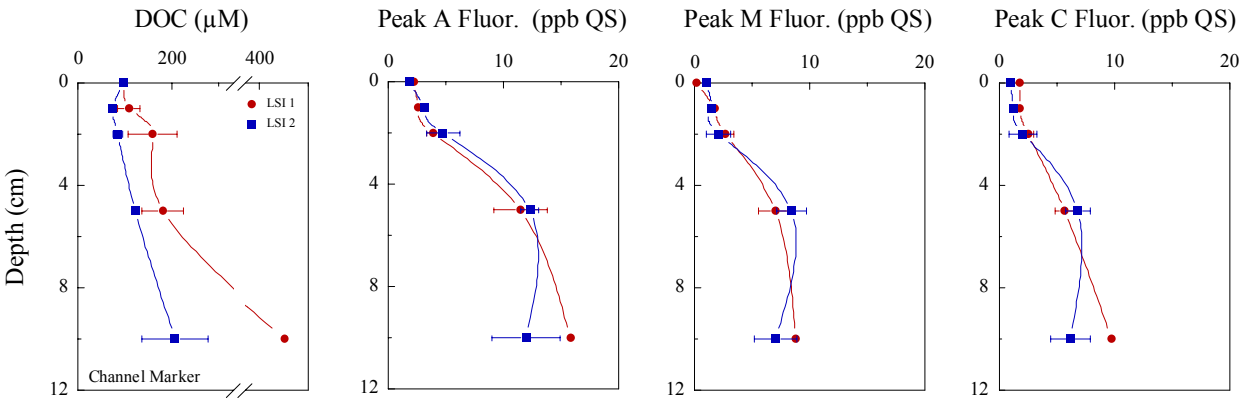

Figure 1 Pore water depth profiles of total DOC and humic-like fluorescence in sediments at the Channel Marker site during LSI 1 (May 1998) and LSI 2 (January 1999). Error bars represent the concentration ranges observed in samples collected at the same sediment depths with replicate sippers. The fluorescence of humic-like peak A is based on peaks observed in EEMS spectra in the region 220-270 nm (excitation) and 410-460 nm (emission). The fluorescence of humic-like peak M is based on peaks observed in EEMS spectra in the region 300-330 nm (excitation) and 390-420 nm (emission). The fluorescence of humic-like peak C is based on peaks observed in EEMS spectra in the region 330-360 nm (excitation) and 420-470 nm (emission).

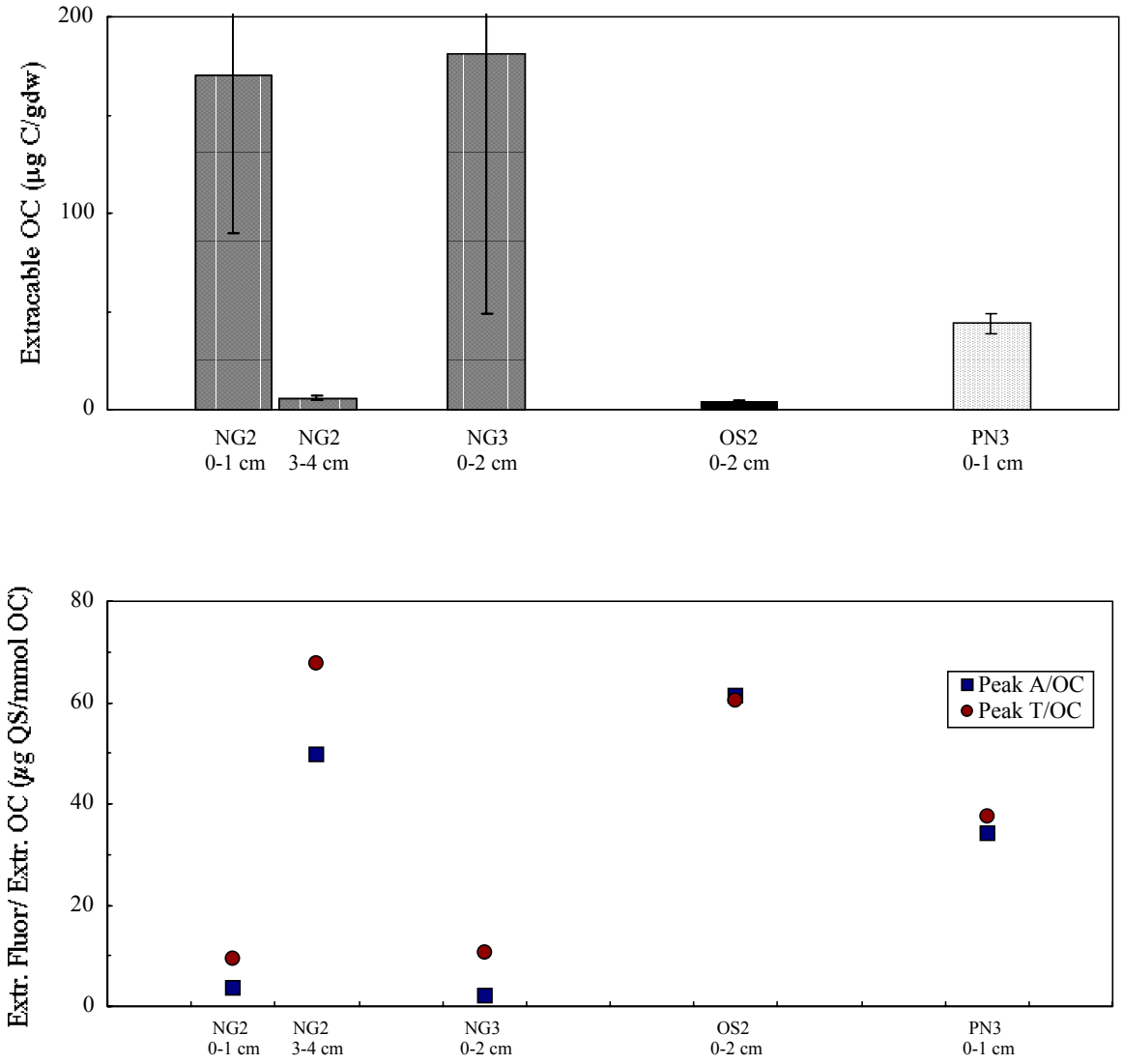

Figure 2 [upper panel] Concentrations of easily extractable organic matter in various sediments from the LSI sites. Note that the Norman's Grapestones (NG) surface sediments have substantially greater amounts of this material than either North Perry Reef (PN) surface algal film sediments or surface sediments from Ooid Shoals (OS). Similar trends are also observed for extractable fluorescent material in these sediments (data not shown here). [lower panel] Concentrations of peak A (humic-like) fluorescence or peak T (tryptophan, protein-like) fluorescence normalized to total organic carbon concentrations in these extracts. For humic-like peaks A and C (the latter not shown here), these ratios are similar to those observed in sediment pore waters, suggesting a relationship between pore water CDOM and this extractable material.

REFERENCES

Berelson W.M., J. McManus, T. Kilgore, K. Coale, K.S. Johnson, D. Burdige and C. Pilskaln. 1996. Biogenic matter diagenesis on the sea floor: A comparison between two continental margin transects. J. Mar. Res. 54: 731-762.

Burdige D. J. 1999. The composition and reactivity of dissolved organic matter (DOM) in marine sediment pore waters. abstract presented at the 1999 ASLO Aquatic Sciences Meeting.

Burdige, D.J. and K.G. Gardner. 1998. Molecular weight distribution of dissolved organic carbon in marine sediment pore waters. Mar. Chem. 62:45-64.

Chen, W. and D.J. Burdige. 1998. Characterization of pore water DOM in marine sediments by fluorescence spectroscopy. EOS 79(1):OS22G (abstr.) and manuscript in prep.

Lakowicz J. R.1983. Principles of Fluorescence Spectroscopy. Plenum Press. New York. 496 pp.

Mayer, L. M., L.L. Schick, and T.C. Loder III.1999. Dissolved fluorescence in two Maine estuaries. Mar. Chem. 64: 171-179.